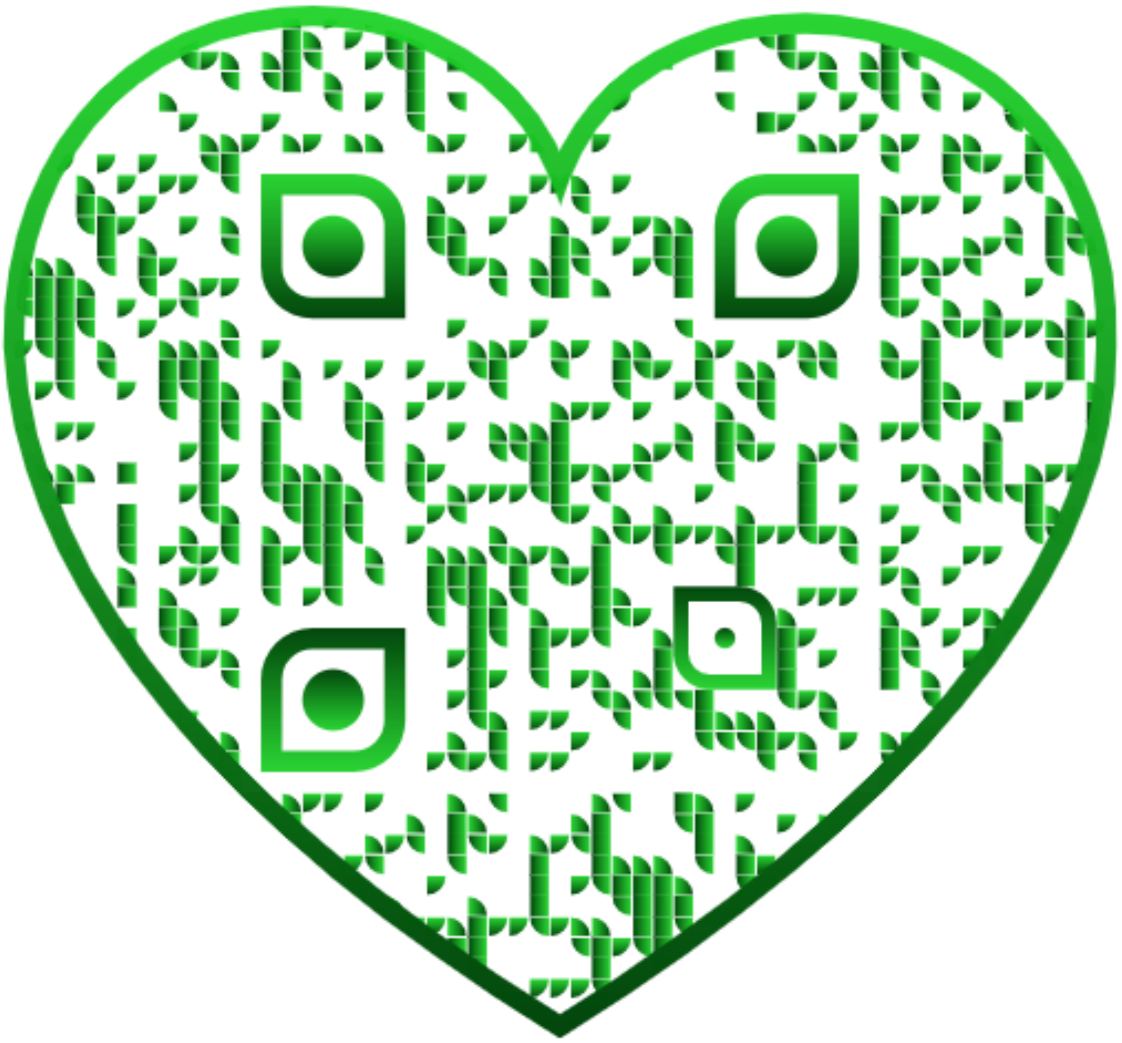
3. Interfacial Phenomena

- **Liquid interface**
- **Adsorption at liquid interfaces**
- **Adsorption at solid interfaces**



Interfacial Phenomena, Introduction

- Interfacial phenomena are the ones that occur at the limit between two immiscible phases, so-called **surface** or **interface**.

- Surfaces or interfaces are boundaries between binary systems, i.e. the boundary between two or more phases existing together.

  - **Surface**: at liquid-air or solid-air interfaces

  - **Interface**: at liquid-liquid, liquid-solid or solid-solid interfaces

- Importance of interfacial phenomena in pharmacy:
  - Adsorption of drugs onto solid adjuncts in dosage forms
  - Penetration of molecules through biological membranes
  - Emulsion formation and stability
  - The dispersion of insoluble particles in liquid media to form suspensions.

Liquid Interface

Surface and Interfacial Tensions

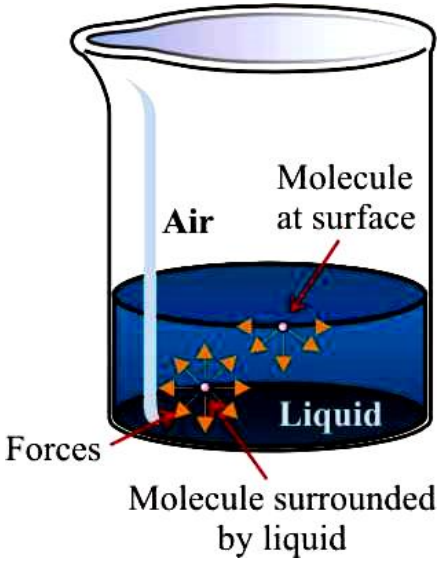
- In the liquid state, the cohesive forces between adjacent molecules are well developed.

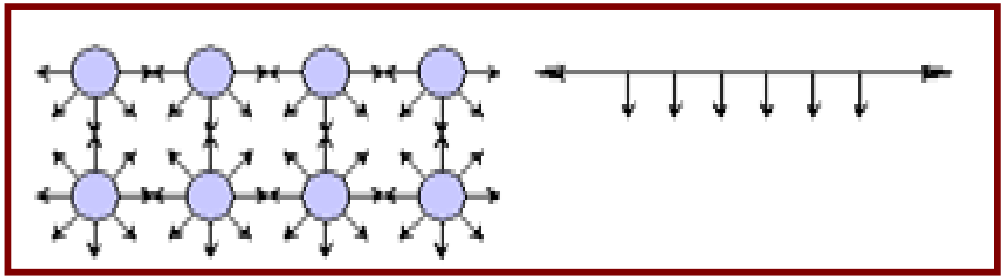
- The properties of the molecules forming the interface are different from those in the bulk that these molecules are forming an interfacial phase.

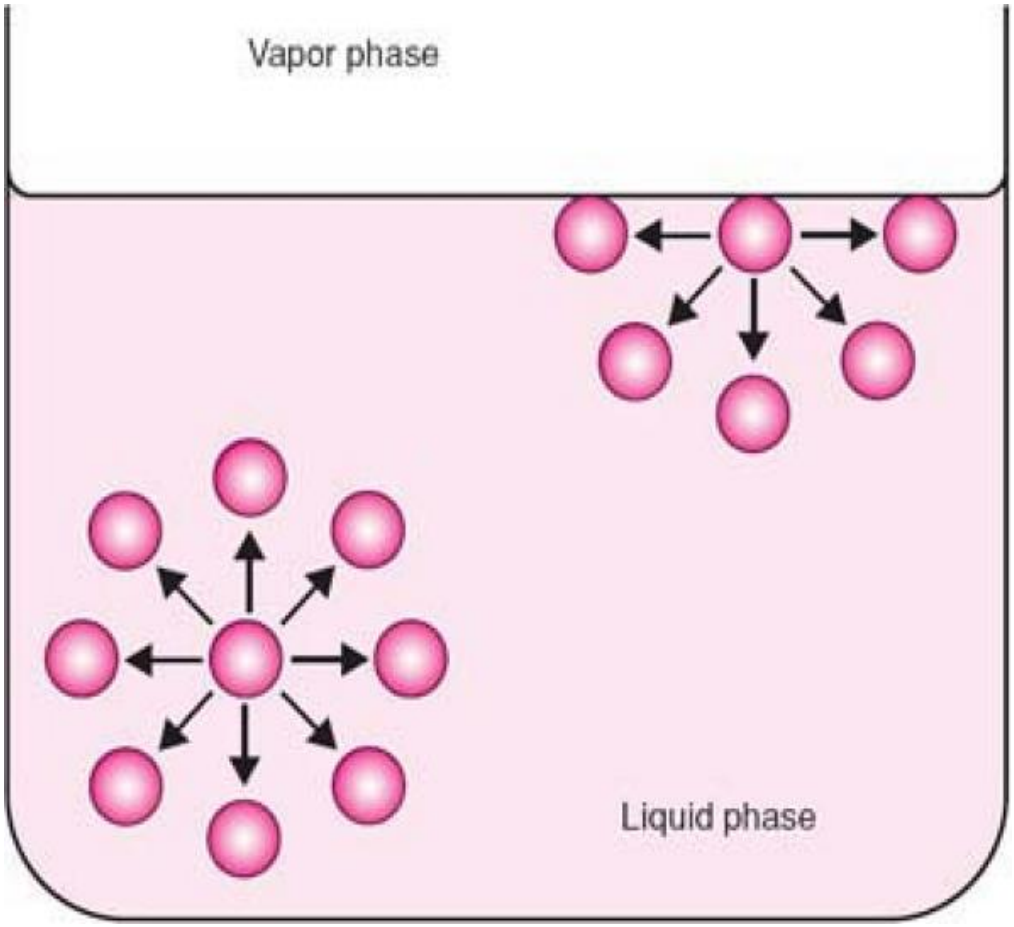
...

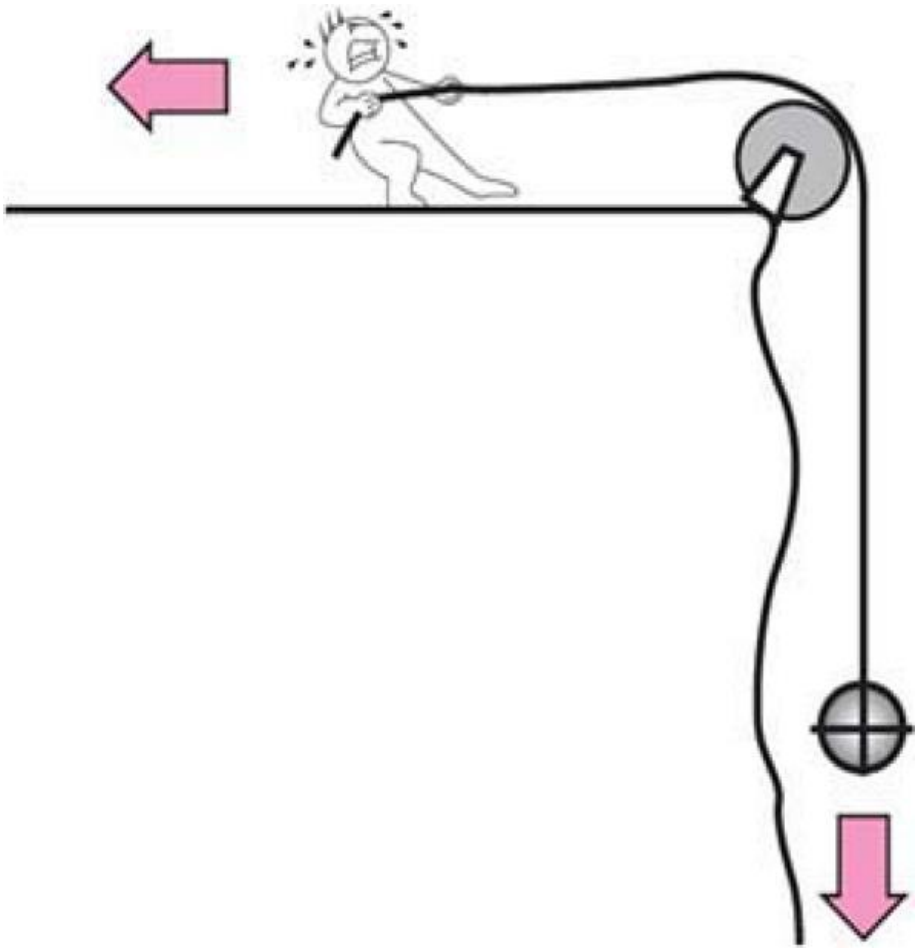
- For the molecules in the **bulk** of a liquid -
  - They are surrounded in all directions by other molecules for which they have an equal attraction.
- For the molecules at the **surface** (at the liquid/air interface)
  - Only attractive **cohesive** forces with other liquid molecules which are situated below and **adjacent** to them.
  - They can develop **adhesive** forces of attraction with the molecules of the other phase in the interface

- The net effect is that the molecules at the surface of the liquid experience an inward force towards the bulk of the liquid and pull the molecules and contract the surface.






Vapor phase
Liquid phase



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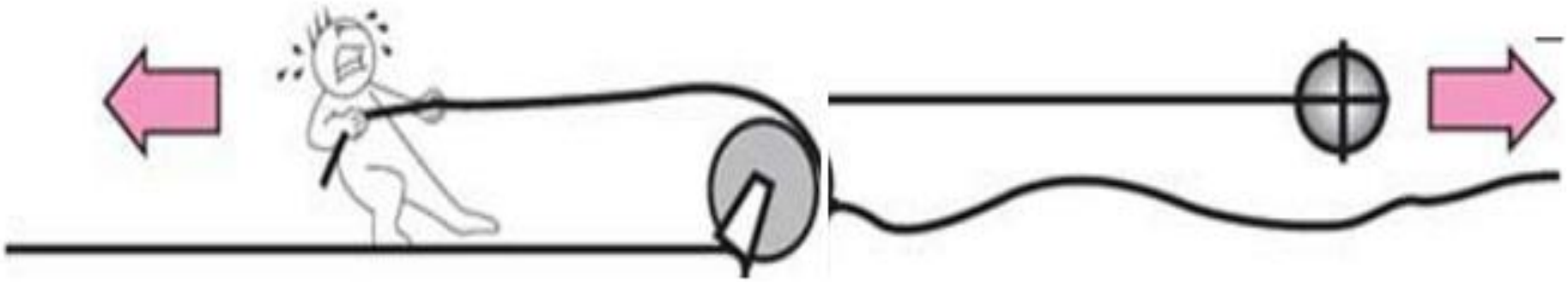

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- To keep the equilibrium, an equal force must be applied to oppose the inward tension in the surface.

- Thus **surface tension** [γ] is the force per unit length that must be applied parallel to the surface so as to counterbalance the net inward pull.

- **Interfacial tension** is the force per unit length existing at the interface between two immiscible liquid phases.

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- Interfacial tensions are less than surface tensions??
- If two liquids are completely miscible, no interfacial tension exists between them.
- Greater surface tension reflects higher intermolecular force of attraction.

...

Surface free energy

- Each molecules near to the surface posses more potential energy as compared to the molecules in the bulk of the liquid.

- Because the molecules at the interface have an unbalanced attractive force, a certain amount of work is required to move a molecule from within the body of the liquid to the interface.

- This work is referred to as surface free energy.

...

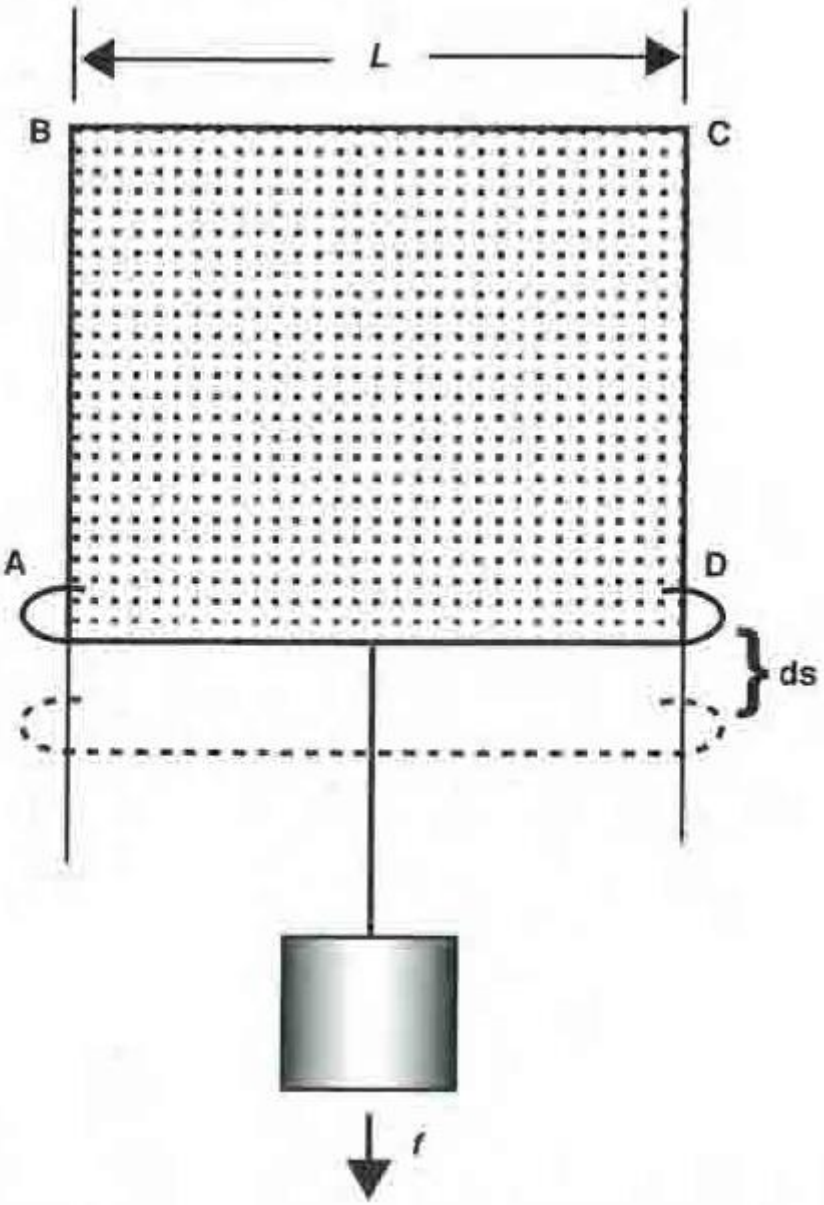
- Surface free energy is defined as the work required to increase the area of a liquid by 1 cm^2.

- If surface of liquid increases, the energy of the liquid also increases as energy is directly proportional to the size of the free surface.

$$dW = f \times ds = \gamma \times 2L \times ds$$

$$dW = \gamma \, \Delta A$$

Note – the surface tension can also be express by the Gibbs free energy (G) (read).


L
B
C
A
D
ds
f

...

- Each molecules of the liquid has a tendency to move inside the liquid from the surface and with minimum surface free energy.
- For equilibrium, the surface free energy of a system must be at a minimum.
  - Thus liquid droplets tend to assume a spherical shape since a sphere has the smallest surface area per unit volume.
- To increase the surface of the liquid work must be done against the surface tension.

...

- Different factors influencing surface and interfacial tensions,
  - **Internal factors** - intermolecular attractive forces?
  - **External factors** -
    - **Electrolytes** tend to increase surface tensions?
    - **Surface active agents** decrease surface tensions?
    - **Temperature** decrease surface tensions?

Measurement of surface/interfacial tension

- Methods for measuring surface and interfacial tension:
  - Capillary rise method
  - Ring (Du Nouy) tensiometer
  - Drop weight method (Stalagmometer)
  - Bubble pressure

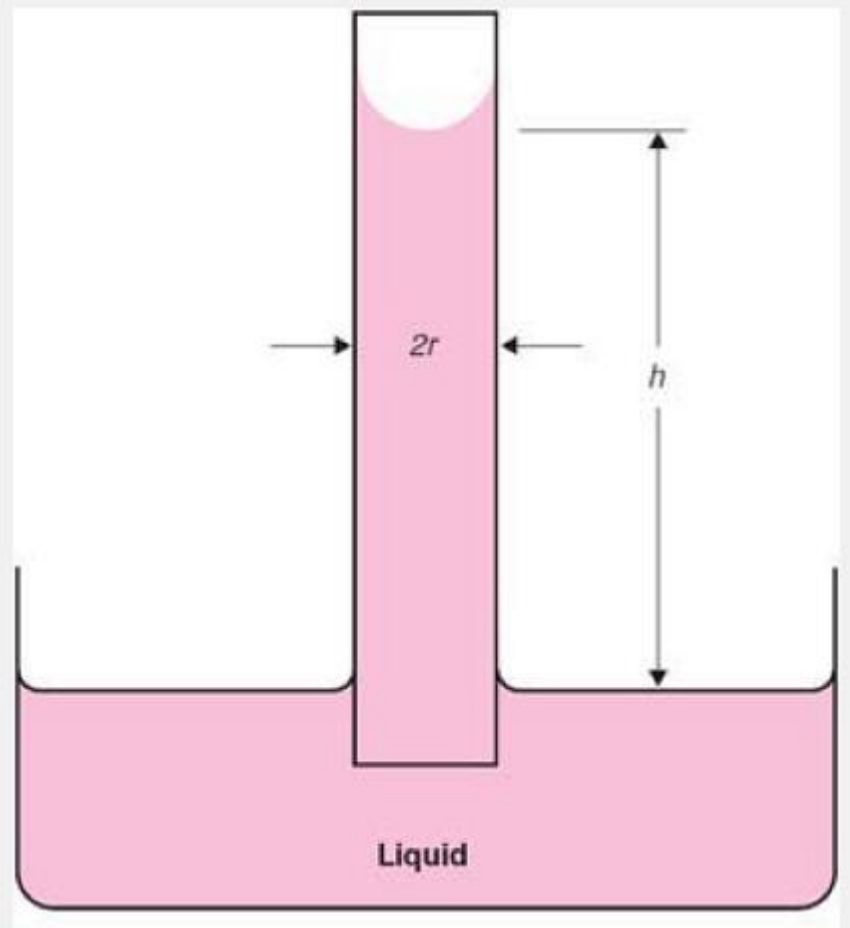
Read

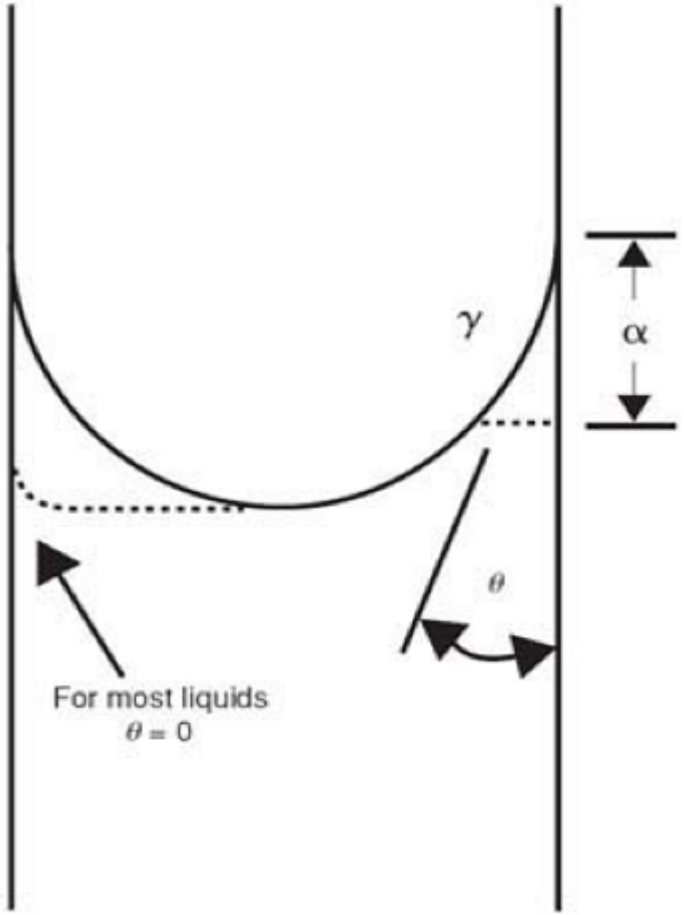
...

- The choice of the method for measuring surface and interfacial tension depend on:
  - Whether surface or interfacial tension is to be determined.
  - The accuracy desired
  - The size of sample

Capillary Rise Method

- When a capillary tube is placed in a liquid, the liquid generally rises up the tube a certain distance.
  - Force of adhesion is greater than the force of cohesion,
  - The liquid is said to wet the capillary wall, spreading over it and rising in the tube,
  - We can measure this rise in a capillary to determine the surface tension of the liquid.


2r
h
Liquid


γ
α
θ
For most liquids
θ = 0

- Consider a capillary tube with an inside radius r immersed in a liquid;
  - The liquid continues to rise in the tube,
  - But, because of the weight of the liquid, the upward movement is just balanced by the downward force of gravity.
  - The upward vertical component of the force resulting from the surface tension:

$$a = y\cos(\theta)$$

- The total upward force around the inside circumference of the tube:

$$2\pi r\,\gamma\,cos\theta$$

- The counteracting force of gravity (mass × acceleration) is given by:

$$\pi r^2\,h(\rho - \rho_0)g + w$$

- The two forces are balanced:

$$2\pi r\,\gamma\,cos\theta = \pi r^2\,h(\rho - \rho_0)g + w$$

Note:

- For water and other commonly used liquids, the angle θ is insignificant, that is, the liquid wets the capillary wall so that cos θ is taken as unity

- The density of the liquid vapor, ρ_0, and the weight of liquid above h in the meniscus, w, are also insignificant.

- Accordingly the surface tension can be calculated:

$$2\pi r\,\gamma = \pi r^2 \text{ x h x } \rho \text{ x g}$$

- Therefore,

$$\gamma = \tfrac{1}{2}\, r \times h \times \rho \times g$$

The DuNoüy Ring Method

- Used for measuring surface and interfacial tensions,
- Principle:
  - The force necessary to detach a platinum–iridium ring immersed at the surface or interface is proportional to the surface or interfacial tension.
  - The force required to detach the ring in this manner is provided by a torsion wire and is recorded in dynes

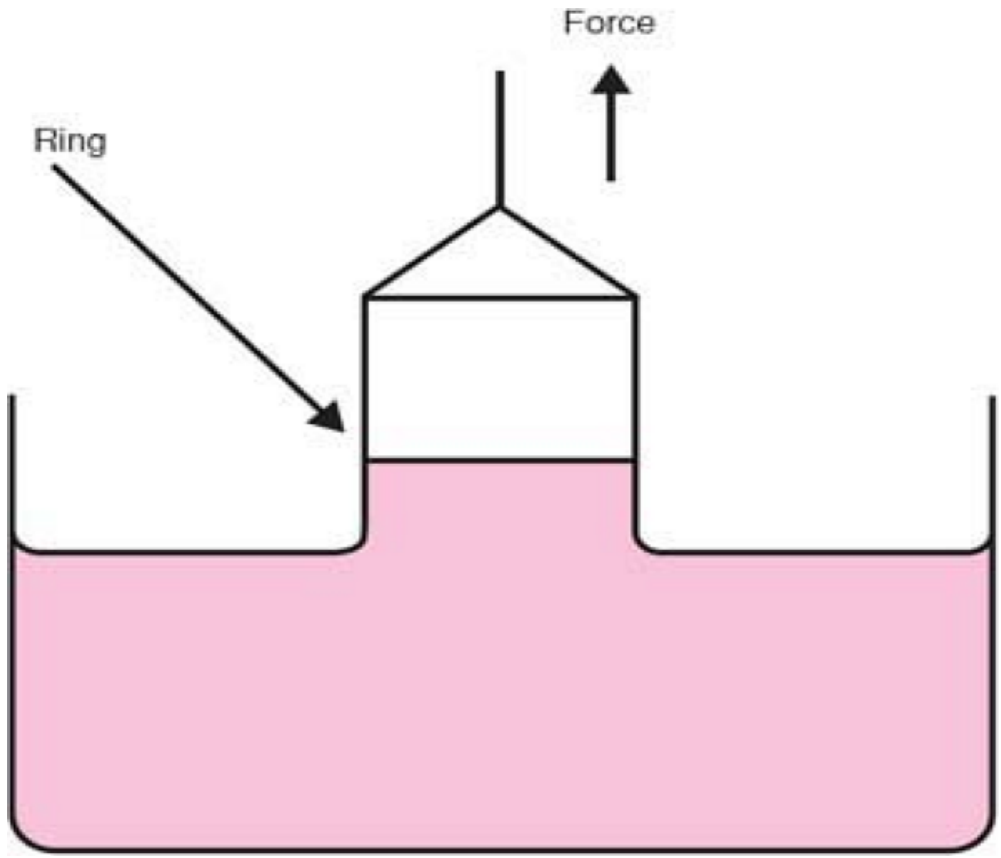


Fig. Schematic of the **tensiometer** ring pulling a column of water above the surface before it brakes away

...

- The surface tension is given by:

$$\gamma = \frac{\text{Dial reading in dynes}}{2 \times \text{Ring circumference}} \times \text{Correction factor, } \beta$$

Spreading and Spreading coefficient

- Consider a drop of oil is placed on the surface of water,
  - It gets mixed/distributed in water??
  - It spreads as a thin film (monomolecular film)??
  - It remains as a drop (duplex film)??

...

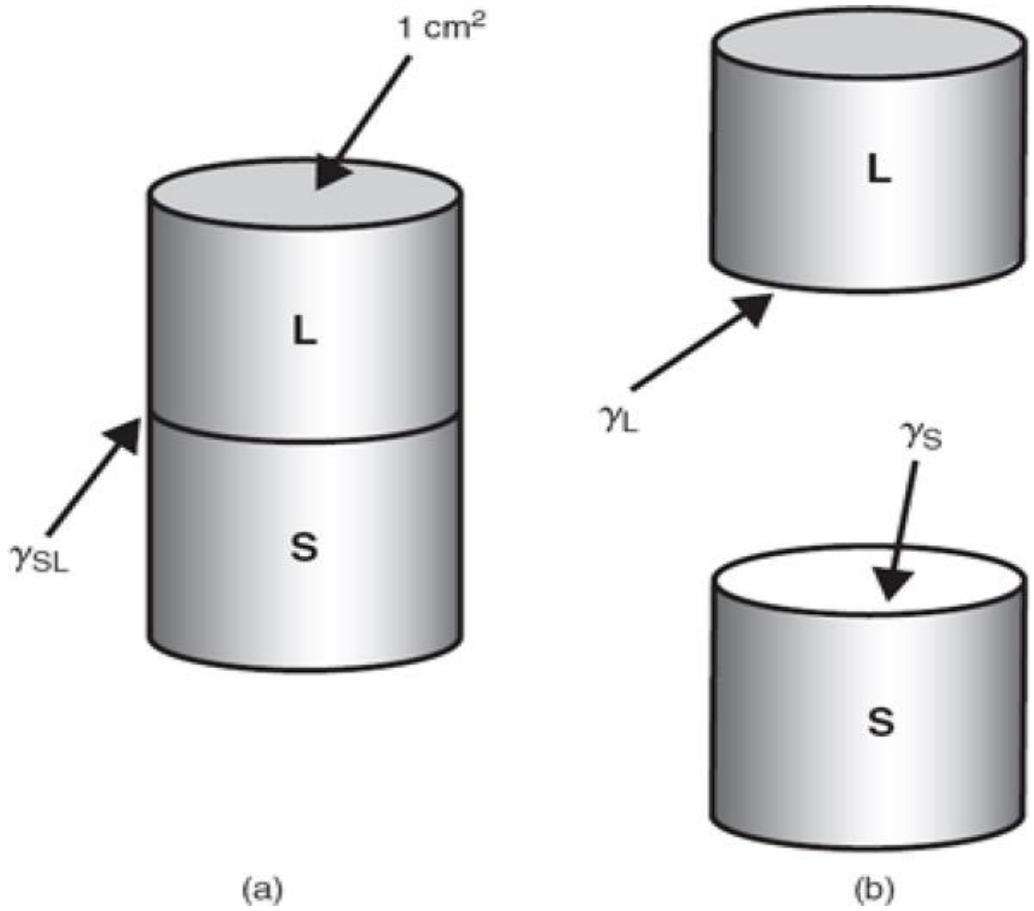
- Duplex films are sufficiently thick (100 Å or more)
  - The surface (boundary between oil and air) and interface (boundary between water and oil) are independent of one another.
- Forces (IMFs)??
  - Cohesive forces between the oil molecules,
  - Cohesive forces between the water molecules,
  - Force of adhesion between the oil molecules and the water molecules.

- Work of adhesion:
  - The energy required to break the attraction between the unlike molecules (Fig below).
  - Surface/interfacial work is equal to surface tension multiplied by the area increment:

Work = Surface tension x ΔA

  - The work required to separate the two sections (work of adhesion), for $\Delta A = 1\ cm^2$:

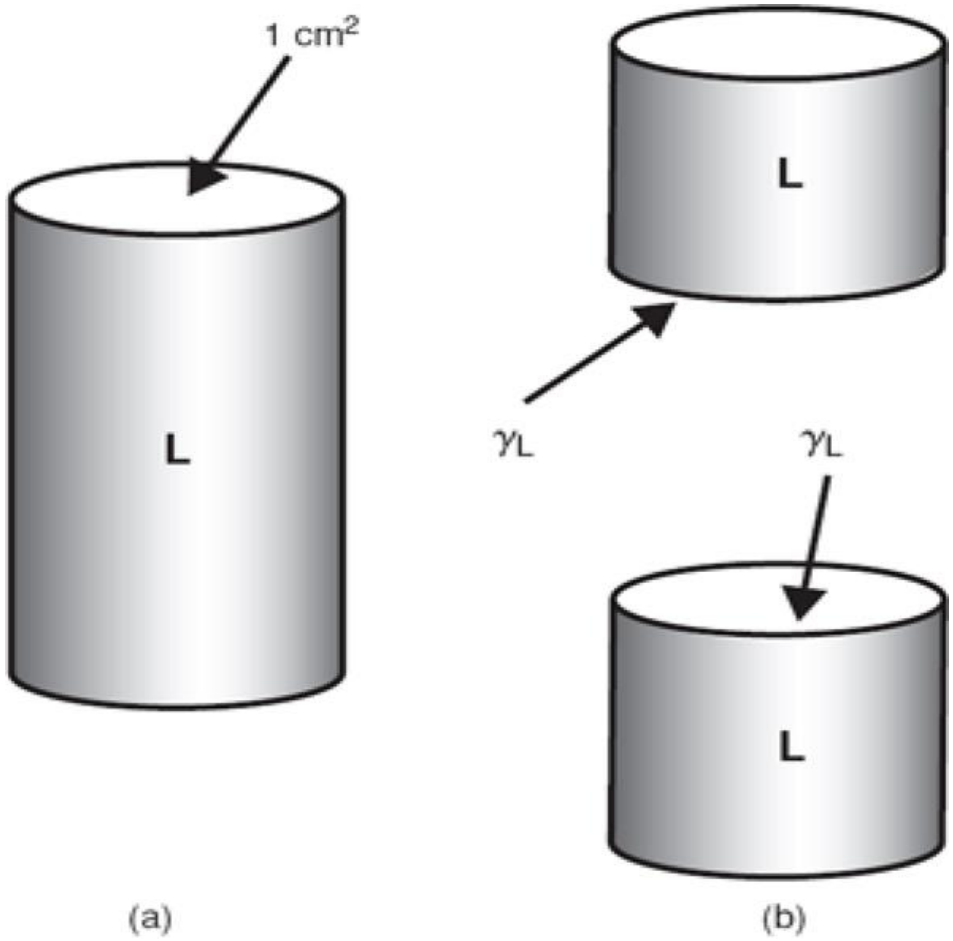
$$W_a = (\gamma_L + \gamma_S) - \gamma_{LS}$$


1 cm²
L
S
γSL
(a)
L
γL
γS
S
(b)

...

- Work of cohesion:
  - The energy required to separate the molecules of the spreading liquid so that it can flow over the sublayer (Fig below),
  - No interfacial tension exists between the like molecules of the liquid,
  - The work required to separate a hypothetical 1cm^2 cylinder of a liquid into two sections, each with a surface tension of γ_L (Work of cohesion):

$$W_C = 2\gamma_L$$


1 cm²
L
L
γL
γL
L
(a)
(b)

- Will the oil spread on a water surface??
  - Spreading occurs if the work of adhesion (a measure of the force of attraction between the oil and the water) is greater than the work of cohesion??
  - The term (W_a - W_c) is known as the spreading coefficient (S):

$$S = W_a - W_C = [(\gamma_L + \gamma_S) - \gamma_{LS}] - 2\gamma_L$$

    - If "S" is positive, the oil will spread over a water surface??

- Rearranging the above equation:

$$S = \gamma_S - \gamma_{LS} - \gamma_L$$

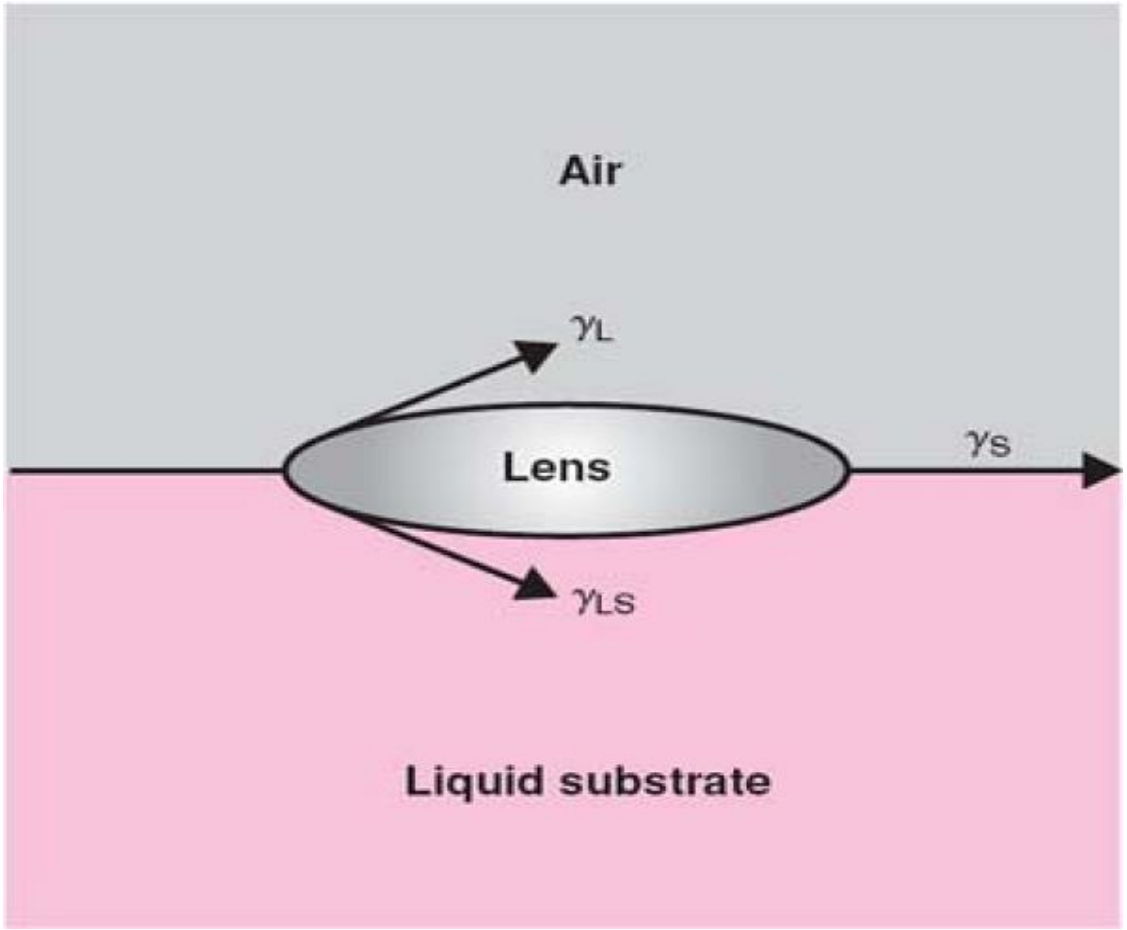
OR

$$S = \gamma_S - (\gamma_{LS} + \gamma_L)$$

Where,

- γ_S ~ surface tension of the sublayer liquid
- γ_L ~ surface tension of the spreading liquid
- γ_{LS} ~ the interfacial tension between the sublayer and the spreading liquid

- Spreading occurs when "S" is positive, i.e. when $\gamma_S > (\gamma_{LS} + \gamma_L)$
- If $(\gamma_{LS} + \gamma_L)$ is larger than γ_S, the substance forms globules or a floating lens and fails to spread.


Air
γ_L
Lens
γ_S
γ_{LS}
Liquid substrate

...

- Spreading can also be described in terms of surface free energy;
  - Spreading occurs if the spreading substance reduces the surface free energy of the system.
  - In other words, spreading occurs if the surface free energy of the new surface and the new interface is less than the free energy of the old surface.

- Note
  - Initial spreading?? (Before equilibrium is reached)
  - After mutual saturation has taken place??

...

- Application of concept of spreading coefficient:
  - Spreading (of semisolids) freely and evenly on the skin,
  - Spreading, HLB (hydrophile–lipophile balance), and emulsion stability,

Adsorption at Liquid Interfaces

- Adsorption occurs when molecules, **dispersed** in the liquid, are partitioned in favor of the interface or in favor of the bulk.
  - Positive adsorption ~ when molecules are partitioned in favor of the interface,
    - Resulting in a corresponding decrease in surface tension??
  - Negative adsorption ~ when molecules are partitioned in favor of the bulk.
    - Resulting in a corresponding increase in surface tension??

- Adsorption Vs Absorption??
  - Adsorption ~ a surface phenomena
    - E.g. concentrating/deposition of molecules on the surface of activated charcoal
  - Absorption ~ where a molecule penetrates into the capillary spaces of the absorbing medium.
    - E.g. taking up of water by a sponge.

Surface-Active Agents (SAAs)

- Substances which absorbed at interfaces (liquid–gas or liquid–liquid interfaces)
- Purpose?
- Synonyms: Surfactants or Amphiphiles or wetting agents?
- Have amphiphilic nature??
  - Both ~ Polar alcoholic group and Non-polar portion

- For the amphiphile to be concentrated at the interface,
  - It must be balanced with the proper amount of polar/hydrophillic and nonpolar/lipophillic groups.
  - If the molecule is too hydrophilic, it remains within the body of the aqueous phase and exerts no effect at the interface,
  - If it is too lipophilic, it dissolves completely in the oil phase and little appears at the interface

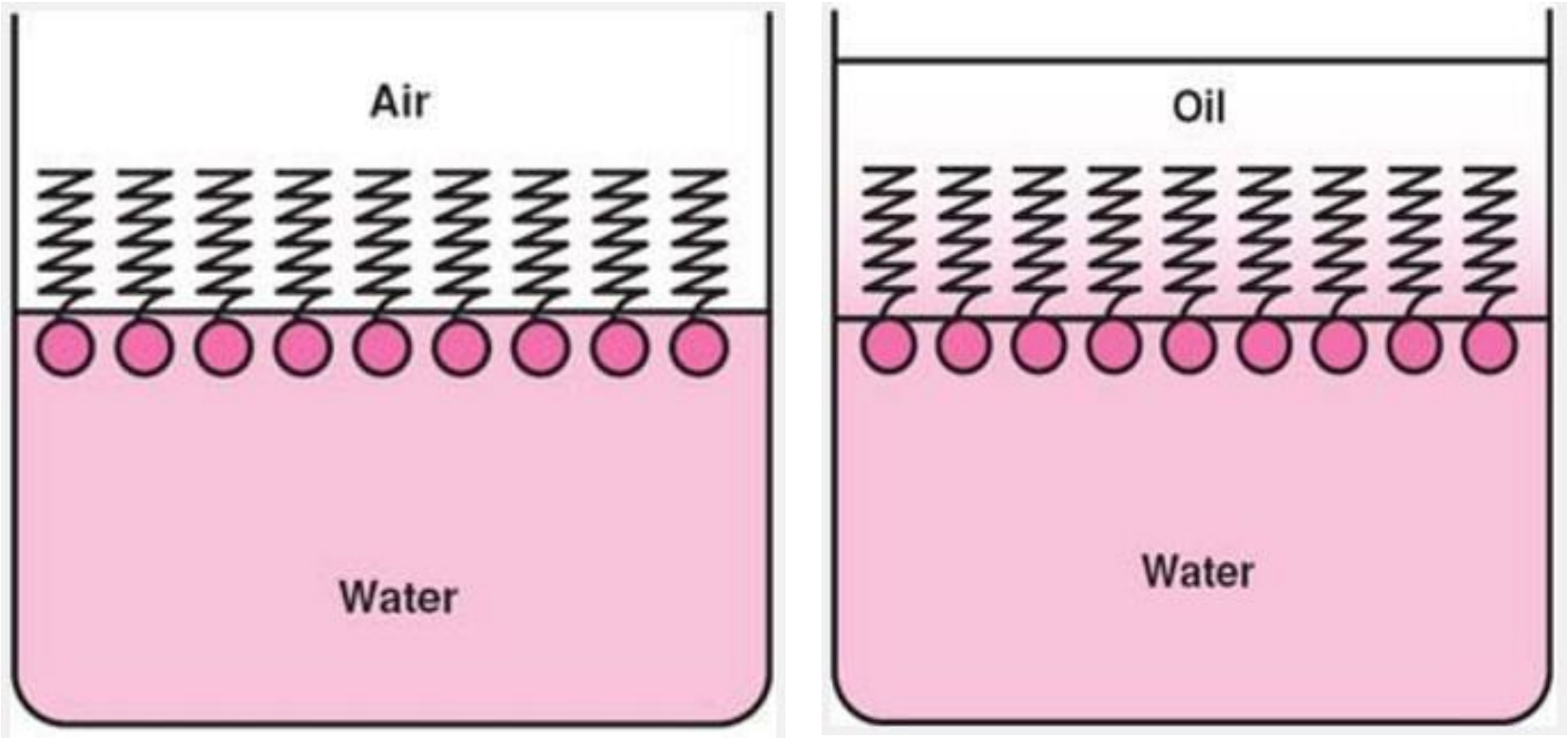


Fig. Adsorption of SAAs at water–air interface and water–oil interface

The HLB System

- Scale of values to serve as a measure of the hydrophilic–lipophilic balance of SAAs.
  - The higher the HLB of an agent, the more hydrophilic it is;
    - E.g. **Tweens**, polyoxyethylene derivatives of the Spans
  - The lower the HLB of an agent, the more lipophilic it is;
    - E.g. **Spans**, sorbitan esters

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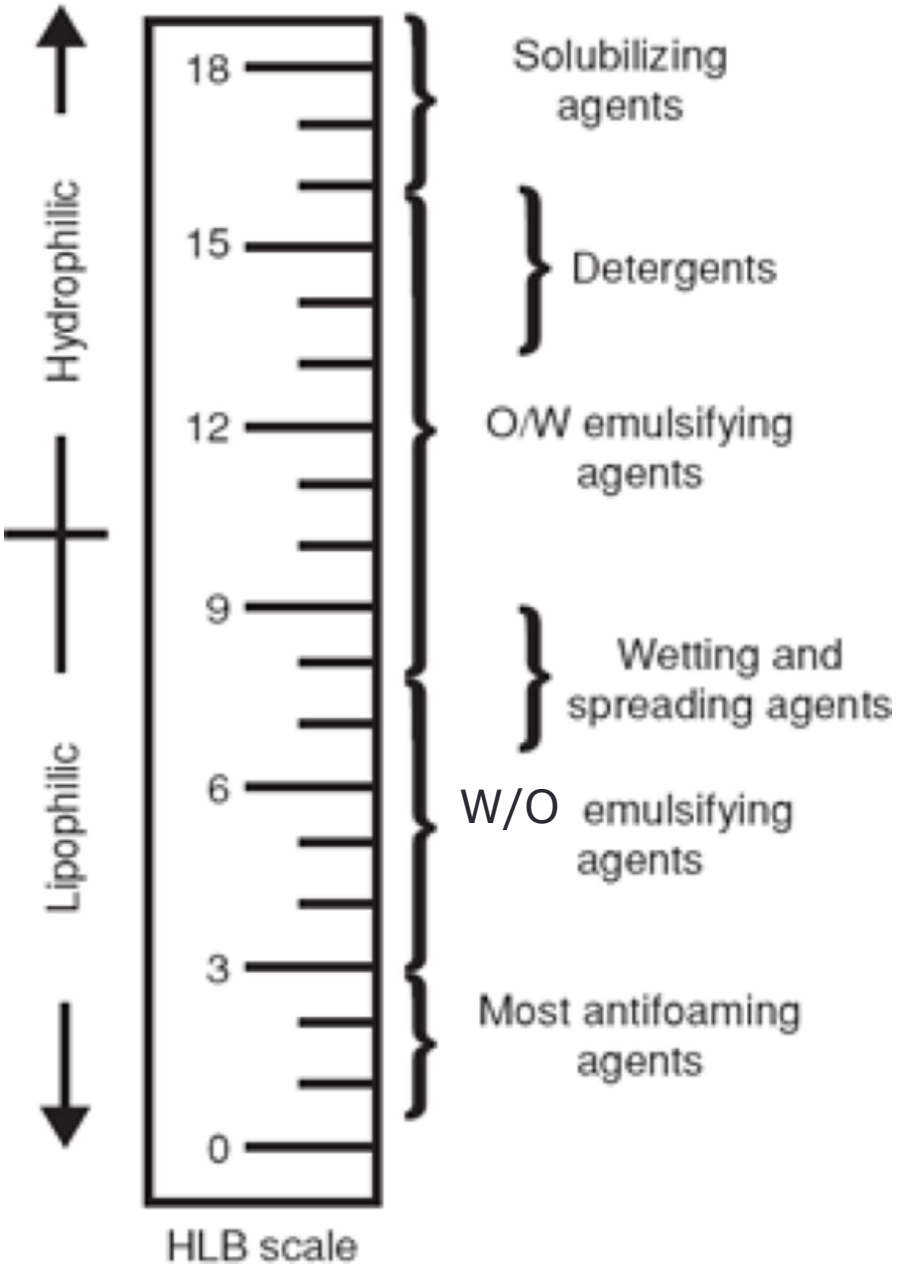


Fig. The HLB Scale

- The HLB of a **nonionic** surfactant w is calculated by:

$$HLB = {}^{E}/_{5}$$

where E is the percentage by weight of ethylene oxide

- On the other hand, the HLB of **ionic** surfactants can be estimated by:

$$HLB = 20\left(1 - \frac{S}{A}\right)$$

where S is the saponification number of the ester and A is the acid number of the fatty acid

- Reading …
  - RHLB = required hydrophilic–lipophilic balance value
  - Soluble Monolayers
  - Insoluble Monolayers and the Film Balance

Adsorption at Solid Interfaces

- Adsorption of material at solid interfaces can take place from either an adjacent liquid or gas phase.
- Applications
  - Gas – Solid adsorption:
    - Removal of objectionable odors from rooms and food,
    - The operation of gas masks,
    - The measurement of the dimensions of particles in a powder

- Solid – liquid adsorption:
  - Decolorizing solutions,
  - Adsorption chromatography,
  - Detergency,
  - Wetting

- Adsorption onto a solid surface Vs liquid surfaces:
  - The surface tensions of solids are invariably more difficult to obtain,
  - Solid interface is immobile in comparison to the turbulent liquid interface
  - The average lifetime of a molecule adsorbed onto a solid surface is longer

...

The Solid–Gas Interface

- Depends on:
  - The chemical nature of the adsorbent and the adsorbate,
  - The surface area of the adsorbent,
  - The temperature, and
  - The partial pressure of the adsorbed gas

...

- Two types of solid-gas adsorption:

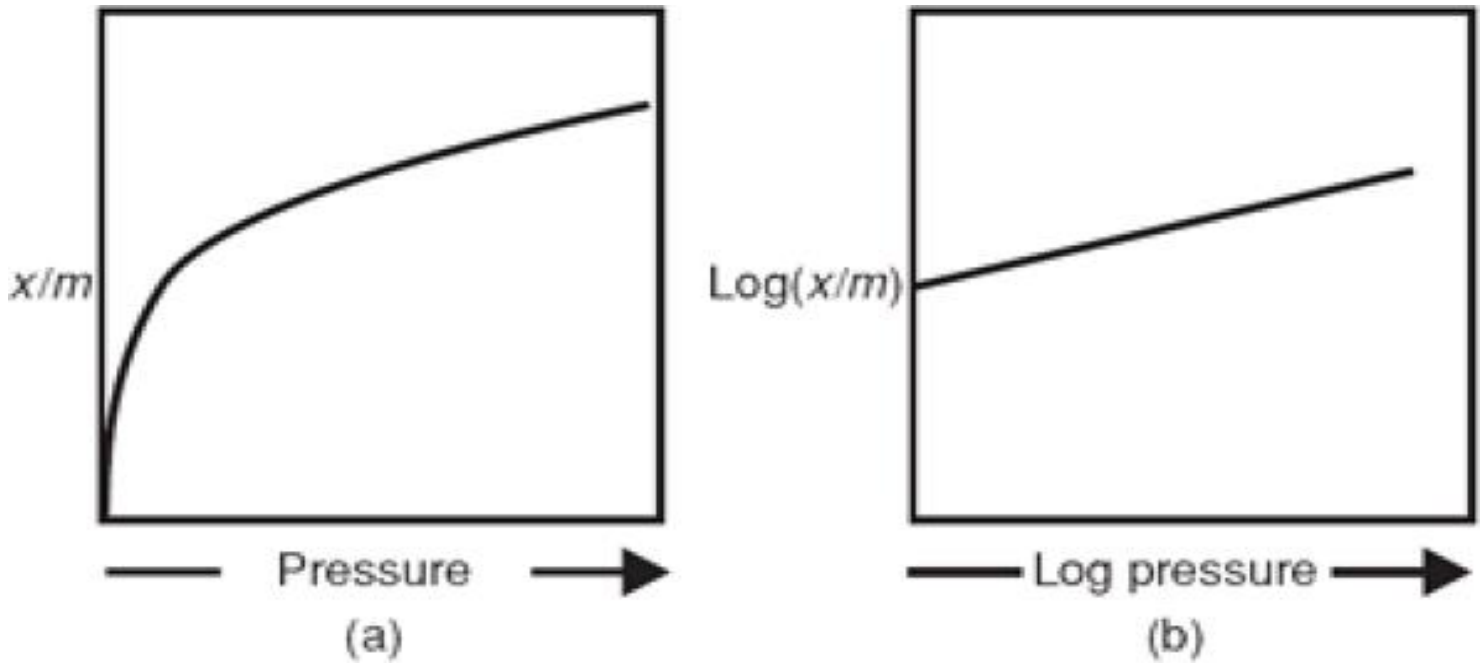
1. Physical adsorption,

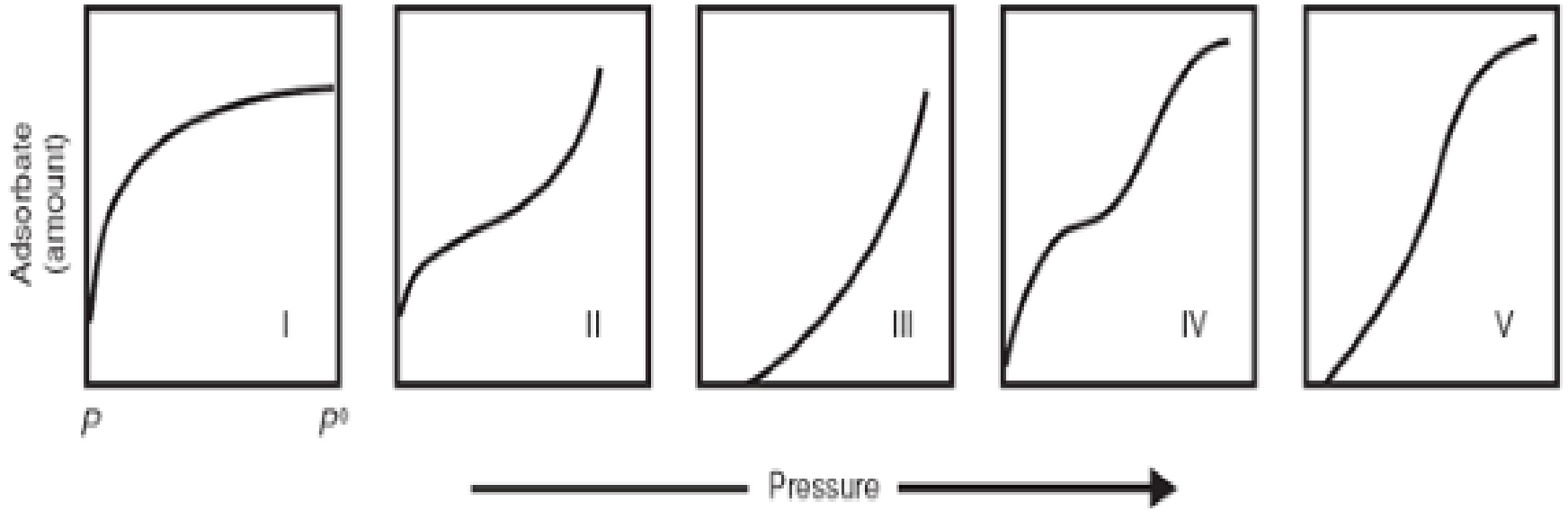
   - Associated with van der Waals forces,
   - It is reversible,
   - Can be desorbed from a solid by increasing the temperature and reducing the pressure.

2. Chemical adsorption or chemisorption

- Attached to the adsorbent by primary chemical bonds,
- It is irreversible unless the bonds are broken.

- Adsorption isotherms
  - Provide the relationship between the amount of gas physically adsorbed on a solid,
    - At equilibrium pressure/concentration at constant temperature yields
  - A plot of moles, grams, or milliliters of gas (x) adsorbed on grams of adsorbent (m) against the equilibrium pressure at constant temperature.
  - Different types: Type I, II, III and IV??


x/m
Pressure
(a)
Log(x/m)
Log pressure
(b)


Adsorbate
(amount)
I
II
III
IV
V
P
P⁰
Pressure

...

The Solid–Liquid Interface

- Analogous to the adsorption of molecules at the solid–gas interface
- Different molecules (organic or inorganic) can be absorbed from solution onto solids such as charcoal and alumina.

...

Activated Charcoal

- Can adsorb enormous amounts of gases or liquids,
- It is a residue from destructive distillation of various organic materials, treated to increase its adsorptive power,
- It is made from material burnt in a superheated high-oxygen atmosphere,
  - Creating small holes in the range of 100 to 800 Å in diameter throughout the grain of the charcoal.
  - This effectively increases the charcoal's surface area
  - The surface area of 1 g of charcoal is approximately 1000 m^2.

...

Wetting and Wetting agents

- When a liquid comes into contact with a solid, the forces of attraction between the liquid and the solid phases plays a significant role.
  - The balance between the forces of attraction of molecules in the liquid and the forces of attraction between the liquid and the solid phases??
    - Governing whether the liquid is able to wet the surface of the solid.

- The most important action of a wetting agent is to lower the contact angle between the surface and the wetting liquid,
- The contact angle is the angle between a liquid droplet and the surface over which it spreads.
- The contact angle may have any value between 0° (complete wetting) and 180° (wetting is insignificant).

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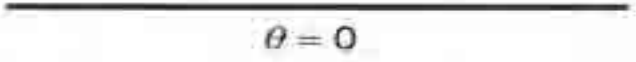
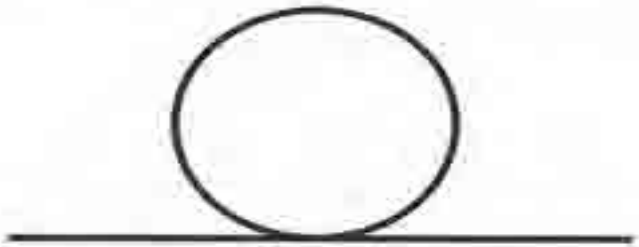
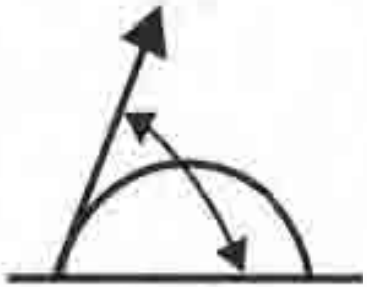


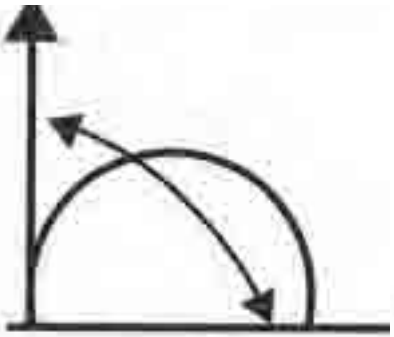
$\theta = 0$



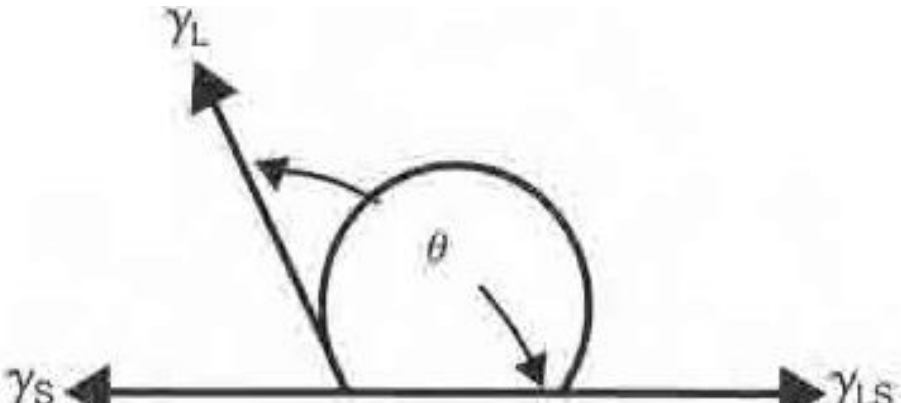
$\theta \rightarrow 180$



$\theta < 90$



$\theta = 90$



$\theta > 90$

- At equilibrium, the surface and interfacial tensions are related by Young's equation:

$$\boldsymbol{\gamma}_S = \boldsymbol{\gamma}_{SL} + \boldsymbol{\gamma}_L Cos\ \Theta$$

- If in the equation, $\boldsymbol{S} = \boldsymbol{\gamma}_S - (\boldsymbol{\gamma}_{SL} + \boldsymbol{\gamma}_L)$, we substitute for $\boldsymbol{\gamma}_S$, we get:

$$\boldsymbol{S} = \boldsymbol{\gamma}_L(Cos\ \Theta - 1)$$

- Or, substitute for $\boldsymbol{\gamma}_S$ in the equation, $\boldsymbol{W}_a = \boldsymbol{\gamma}_L + \boldsymbol{\gamma}_S - \boldsymbol{\gamma}_{SL}$, we get:

$$\boldsymbol{W}_a = \boldsymbol{\gamma}_L(1 + Cos\ \Theta)$$

Applications of Surface-active Agents

- Surfactants (SAAs) can be used as:
  - Emulsifying agents
  - Wetting agents
  - Solubilizing agents
  - Detergents
  - Antibacterial and other protective agents
  - Aids to the absorption of drugs in the body.

...

- A surfactant may affect the activity of a drug.
  - E.g. The penetration of hexylresorcinol into a pinworm is increased by the presence of a low concentration of surfactant.
- SAAs (Quaternary ammonium compounds) may possess antibacterial activity.
  - The agents are adsorbed on the cell surface and supposedly bring about destruction by increasing the permeability or "leakiness" of the lipid cell membrane.

- Note

  - Both gram-negative and gram-positive organisms are susceptible to the action of the cationic quaternary compounds, whereas anionic agents attack gram-positive organisms more easily than gram-negative bacteria.

  - Nonionic surfactants are least effective as antibacterial agents.

...

- Surfactants and bile salts may affect the gastrointestinal absorption of antibiotics.
  - Polyoxyethylene lauryl ether reduced the absorption of propicillin in the stomach and increased it in the small intestine.
- Some surfactants increase the rate of intestinal absorption, whereas others decrease it.
- Some of these effects may result from alteration of the membrane by the surfactant.

...

Foams and Antifoaming Agents

- Any solutions containing SSAs (soaps) produce stable foams when mixed intimately with air.
- A foam is a relatively stable structure consisting of air pockets enclosed within thin films of liquid stabilized by a foaming agent.
- Agents that break the foam and are known as antifoaming agents (e.g. alcohol, ether, castor oil).

...

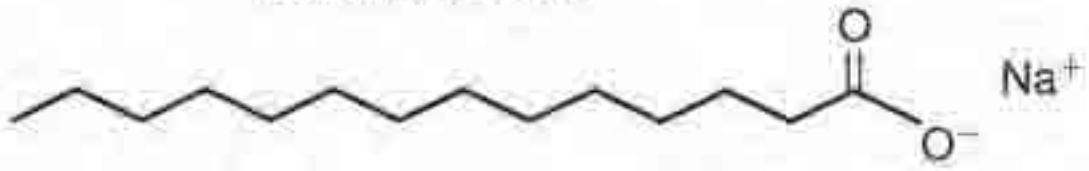
- Foams are sometimes useful in pharmacy (e.g. , Vaginal contraceptive or antimicrobial formulations)
- The undesirable foaming of solubilized liquid preparations poses a problem in formulation.

...

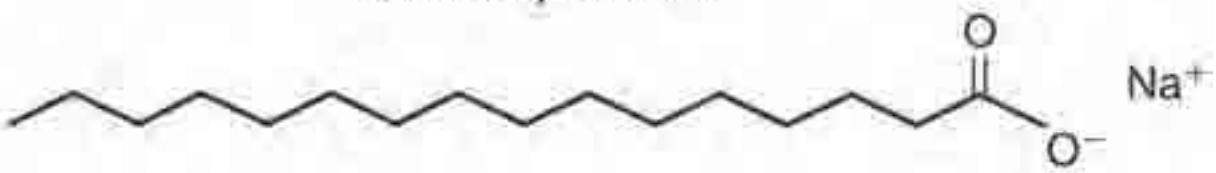
Soaps

- All of the soaps are fatty acid salts (anionic surfactant).
- They are characterized by:
  - A long hydrocarbon chain, which may be
    - **Monounsaturated** (i.e. have one double bond), **Polyunsaturated** (i.e., have more than one double bond), or **saturated** (i.e., no double bonds),
  - A carboxylate group at the end

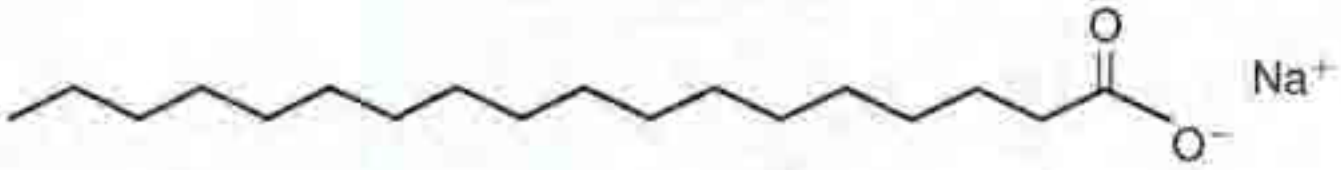
Sodium myristate



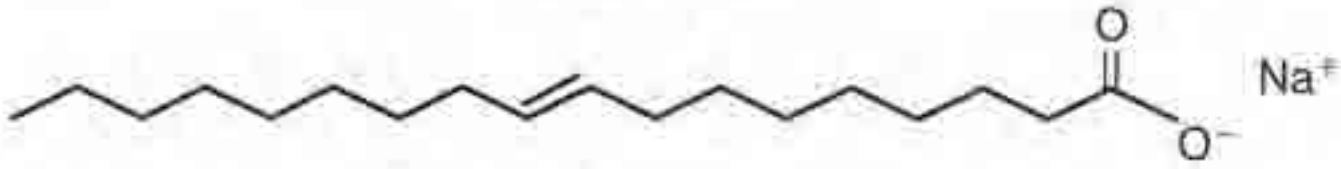
Sodium palmitate



Sodium stearate



Sodium oleate



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- Detergency is a complex process of removing of foreign matter from surfaces.

- The process involves:
  - The hydrocarbon tails of the detergent anions dissolve in the grease,
  - The grease spot gradually breaks up and becomes pincushioned by the detergent anions; and
  - Small bits of grease are held in colloidal suspension by the detergent.
  - The anionic heads keep the grease from coalescing because the particles carry the same electric charge.

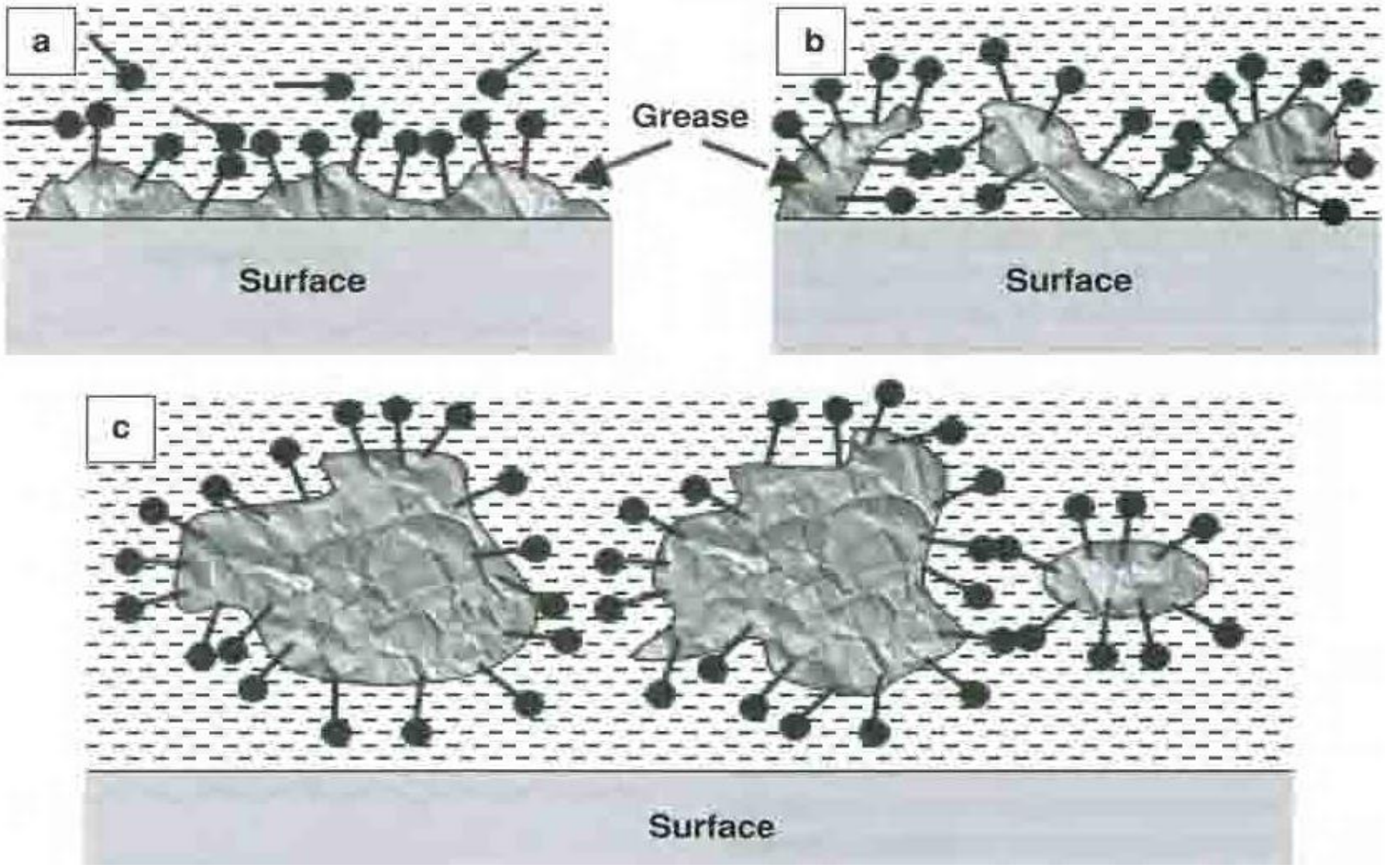

Fig. Mechanism of detergent action

- Note: Lung surfactant
  - A SAA that covers the surface of alveoli contacted with air.
  - It decreases the surface tension at the air-alveoli interface.
  - Two main tasks:
    - It prevents the collapse of alveoli.
    - Decrease the pressure inside the alveoli